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(54) Title: COLD PROCESSES FOR PREPARING GLASS THROUGH THE USE OF A CRYSTALLINE SILICATE MATRIX				
(57) Abstract <p>The present invention discloses a process for solid waste encapsulation in forms suitable for long term storage and transportation as well as a process for handling inadvertent toxic or radioactive releases and accidents. The glassification of toxic and radioactive wastes in a stable, water resistant solid by a process that does not require subjecting the waste to harsh conditions of elevated pressures and temperatures or a drastic increase in either volume or weight is described. Novel materials based on this silicate composition are also disclosed.</p>				

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DESCRIPTIONCOLD PROCESSES FOR PREPARING
GLASS THROUGH THE USE OF A
CRYSTALLINE SILICATE MATRIX

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BACKGROUND OF THE INVENTION

10 This application is a continuation-in-part
application of Serial No. 08/275,837, filed July 15,
1994.

FIELD OF THE INVENTION

15 The present invention relates to a process of
forming glass and related silicate compounds. This
invention also relates to a process for vitrifying waste
materials, including radioactive wastes, and for handling
chemical spills and accidental releases of radioactive
20 materials. Another aspect of this invention is the
preparation of novel silicate foam-like materials.

DESCRIPTION OF THE RELATED ART

25 Much attention has been given in recent years to the
problems associated with the transportation and storage
of toxic wastes. However, despite the enormous effort
expended, there is still an urgent need to develop
economical ways to solidify toxic wastes into a form that
30 will facilitate waste transportation as well as providing
an encapsulated waste product that will be resistant to
leaking or leaching into the environment. Many of the
approaches in this field have relied on high temperature
processes. These processes are not only expensive,
35 impractical and limited in scope in their application but
also potentially hazardous as they require the heating of
toxic, volatile and even explosive mixtures.

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These problems are particularly evident in the case of radioactive wastes. For example, slightly enriched uranium nuclear fuel used in a light water reactor of a nuclear power plant is reprocessed to recover unburned ^{235}U and formed ^{239}Pu in a spent fuel. In this treatment, in general, the spent fuel is dissolved in nitric acid to recover U and Pu by a wet process and thereafter remains as quite high-level liquid radioactive waste containing at least 99% of fission products and a small amount of actinides such as ^{241}Am and ^{244}Cm .

This liquid waste has a radioactivity of at least 10^6 Ci per ton of the uranium fuel and contains at least 1 Ci of radioactive substances per ml of the liquid, emitting harmful radiation for a period of as long as 10^3 to 10^6 years. This liquid waste is also approximately a 2N nitric acid solution containing corrosion products as well as suspended materials and precipitates. In addition, the decay of the radioactive elements in the solution generates heat and, therefore, it must be stored in a stainless steel tank having stirring and cooling means. Such storage is also quite dangerous over a long period of time. Solutions which are intended to be stored for long periods are generally neutralized with sodium hydroxide. These neutralized solutions then become water soluble nitrate salts which have a high pH in order to prevent corrosion in standard steel tanks.

Most investigations have been made on the solidification processes of high-level liquid waste using borosilicate glasses. The use of borosilicate glasses involve complicated and expensive processes for the vitrification of only select wastes materials. Borosilicate waste glasses are characterized by good glass forming properties but poor chemical durability. Conversely, glass compositions having excellent chemical durability, such as obsidians and nepheline syenite,

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require such high formation temperatures when made by conventional processing methods that they have been largely eliminated from consideration as a solid waste form. Unusually high glass forming temperatures increase
5 the likelihood of undesirable offgassing of radioactive waste materials during the waste and glass mixing stage.

Iler notes that most synthetic silicates are amorphous when precipitated from an aqueous solution as
10 opposed to all naturally occurring silicates which are crystalline. The amorphous nature of synthetic silicates is apparently due to many factors, such as inconsistent sizes of the polysilicates in an aqueous solution, rapid polymerizations to polysilicates promoted by pH changes
15 often occurring upon metal salt addition, and the formation of polymeric basic metal ions or colloidal metal hydroxides caused by pH changes in the locality of the metal ions. Since polysilicates are present in a broad range of sizes, they cannot arrange themselves into
20 a regular crystal lattice with the metal ions. The requirement or desirability of a crystalline silicate as opposed to an amorphous silicate is therefore linked to, at some point in a production process, the degree of homogeneity of the reactants prior to their reaction
25 commencing. A more accurate depiction of the gellification of polysilicates often accompanying metal salt addition is the adsorption of metal ions onto gelatinous silica or as a mutual coagulation of the positively charged colloidal metal hydroxide and
30 negatively charged colloidal silica. Therefore, if crystalline silicate is desired, the polysilicates must be kept uniform and small in size and the addition of metal salts should be controlled so as not to promote rapid pH changes either in the solution as a whole or in
35 the locality of the metal ions.

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In U.S. Patent No. 4,376,070 Pope et al. disclose a method of immobilizing nuclear waste comprising preparing a glass which comprises about 30% to about 85% of silicon compounds, about 5% to about 30% of sodium compounds, up to 30% of an aluminum compounds, and 5 to 30% of a boron, calcium, or magnesium compounds. This glass is able to vitrify up to an equal weight of nuclear waste. Unfortunately, this vitrification process suffers from the requirements of initial drying at 500°C and then heating at temperatures of from 800 to 1300°C.

In U.S. Patent No. 4,377,507 Pope et al. describe a similar hot glass vitrification with an alumina silicate glass. This process requires high temperatures and up to 40% of alumina in the glass composition and does not provide a mild process for the vitrification of potentially unstable and explosive wastes.

In U.S. Patent No. 3,959,172 Brownell et al. disclose the immobilization of radionuclides in insoluble metallosilicates. One aspect mentioned is the ability to encapsulate cesium in an aluminum silicate, the molar ratio of cesium, aluminum, and cesium was 1:1:2, to form a synthetic pollucite. This process produced very insoluble, fine crystals. A major problem with this approach is the very small particle size of the resultant cesium containing crystals. This small particle size would not be conducive to the long-term storage and transportation of radioactive wastes. Additionally this process requires subsequent calcination at high temperatures to lock the cesium atoms into a cesium aluminosilicate lattice.

In more recent developments, Wakabayashi et al. in U.S. Patent 4,514,329 describe a process for vitrifying radioactive waste comprising dissolving a water soluble vitrifying-facilitation inorganic compound into a liquid

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radioactive waste acidified with nitric acid, adding an alcoholic silica sol, allowing the resulting solution to gel at from room temperature to 50°C, calcining the resulting gel by microwave radiation, heating the
5 calcined product, and cooling it to obtain the vitrified product. This process also requires high temperatures for the production of vitrified waste materials.

Various cementaceous materials have also been
10 employed in the vitrification of wastes. The most widely studied being the Portland cements, calcined calcium based materials. The use of cements for solidification does not require high temperatures. However, use of commonly known materials suffers from the large weight
15 and volume increases necessary to get a stable solid (1000% to 2000%). Further, the cementaceous processes common today are characterized by additions of much less water and the absence of sodium compounds as opposed to some of the compositions advanced herein. Current
20 cementaceous processes tend to form compositions with high carbonate concentrations which are less stable with prolonged exposure to radiation than silicate compositions.

25 Another goal of the present invention is to develop inorganic silica based materials with unique physical properties, similar to those ascribed to the silica "aerogels". Aerogels are highly porous, very low density solid foams with very tiny pore and particle sizes that
30 form an open-cell structure. Aerogels have been prepared by replacing the liquid solvent in a "wet" gel with air. The first aerogels were silica based and were made during the 1930's by Peter Kistler at Stanford University.

35 The potential commercial applications for silica aerogels stem from their outstanding thermal insulating, acoustical, and dielectric properties. Lawrence

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Livermore National Laboratory claims that these materials will have utility for insulation, solar covers, refrigeration, fire retardant materials, sound impedance matchers, shock absorbers and dampeners, speaker box acoustics, sonic range finders, and as materials for electronic components. However, as of 1991 aerogels had only been commercially produced in Sweden for use in nuclear particle detectors. This is mainly due to practical considerations in the preparation of these aerogels. Their preparation is quite laborious and has yet to be produced economically on a commercial scale.

Vitrified waste products must have an excellent chemical durability and high homogeneity. To satisfy these requirements, it is generally appropriate to use materials with a high silica content. However, silica-rich materials have a melting temperature far higher than materials having a low silica content. Homogenization of mixtures at high temperatures is complicated by non-equilibrium events, such as sublimation of uncombined oxides, specific reaction between wastes and silica to give metastable high volatility melts, and phase separation by density difference. Even the most intimate mechanical mixing of waste and glass forming components cannot always circumvent these problems. High temperatures should also be avoided in the vitrification of radioactive wastes as many radioactive compounds, such as PuO_2OH_2 and AmO_2OH_2 , have low but measurable volatilities under conditions generally employed for "hot", thermal or microwave, vitrification processes (Krikorian et al., 1993). Such temperatures must also be avoided in the treatment of wastes that may contain flammable, volatile or explosive species. These "hot" processes are also expensive, impractical, and complicated. Thus, there is a significant need to develop a versatile means of solidifying liquid wastes

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into a stable form for transportation and disposal that would not require high temperatures and pressures.

SUMMARY OF THE INVENTION

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The present invention is addressed to solving one or more of the problems inherent in the prior art by disclosing a process for solid waste encapsulation in forms suitable for either long-term storage or transportation as well as a process for handling inadvertent toxic or radioactive releases and accidents. This present disclosure also provides for the preparation of novel silica based inorganic materials via an efficient, inexpensive, and versatile method.

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The present invention encompasses the ability to encapsulate toxic and radioactive wastes in a stable, water-resistant solid by a process that does not require subjecting the waste to harsh conditions of elevated pressures and temperatures or a drastic increase in either volume or weight. Surprisingly, the present invention is also able to accommodate very high concentrations of sodium and corrosives. Additionally, various organic and inorganic materials can be added to this silicate composition to impart desired properties to the vitrified waste. For example, radiation blockers, such as bismuth oxide and lead oxide, can be added to compositions that will be used to encapsulate radioactive waste. This will impart an enhanced ability to block α , β , γ , and X-rays that would otherwise be released into the environment and will result in increased safety in the handling, storage, and transportation of these wastes.

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Other methods exist for producing materials for alkali silicates than those discussed herein. These other methods are distinguished from the methods of this

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invention by the methods and concentrations employed as well as the curing processes. Other references, such as Japanese patent Kokai application 49-59828 (1974), propose the use of additives for altering the

5 characteristics of alkali silicates without addressing or disclosing the importance of using a carrier solvent (i.e., a polar organic solvent). Addition of solvents, acids, bases, metal oxides, metal salts and organic

10 materials produce entirely different effects and create materials with substantially different characteristics when not employed according to the methods of the present invention. Generally the other methods produce materials that are either nonhomogeneous or are granular. Either

15 one of these qualities is generally undesirable for the applications stated for the compositions described in accordance with the present invention and these drawbacks are likely responsible for the lack of any significant commercial success of the other materials. In contrast,

20 the present inventors have found that organic polar solvent plays an important role in introducing the additive prior to mixing or combining the additive with the alkali silicate. The methods of the present invention offer an innovative approach to introduce additives, primarily reactive additives, into alkali

25 silicates without producing granular or significantly nonhomogeneous materials.

An embodiment of the present invention is a method of preparing a silicate composition. This method

30 comprises preparing an aqueous composition of an alkali silicate, with or without urea, to form a silicate solution; adding to the silicate solution a composition comprising a polar organic solvent and an aluminum-containing Lewis acid to form an admixture; and mixing

35 the resulting admixture to form the silicate composition.

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In this aspect of the present invention the term "silicate composition" is used to refer to the material produced in accordance with the above mentioned process. This silicate composition will initially form a gel, a semisolid mass of colloids in which the dispersed phase has combined with the continuous phase, which upon dehydration and curing will form a stable solid. Therefore, this silicate composition can be referred to as either a gel or a solid depending on the amount of moisture it contains and the conditions of the curing process it has undergone.

The term "curing process" refers to the chemical process of preserving or finishing the silicate composition. In the present case, curing is accomplished by letting the silicate composition set for an appropriate length of time at an appropriate temperature. If the silicate composition is going to be used for the vitrification of waste materials then it is cured by allowing it to set at from about 40°F to about 150°F, for up to several months or longer depending on its exact composition. If the silicate composition is going to be used to prepare a foam, then it only needs to be cured for several minutes before it is dewatered.

In this aspect of the invention the term "alkali silicate" is used to refer to solutions of alkali metal silicate glasses which have been dissolved in water. Alkali metal silicate glasses are generally prepared by processes that are well known in the art. For example, alkali metal silicate glasses can be synthesized by melting an appropriate alkali metal salt, such as an alkali metal oxide, sulfate, or carbonate (eg. Na_2O , Na_2SO_4 , Na_2CO_3 , K_2O , Li_2O and the like), and silicon dioxide. The weight ratio of silicon dioxide to alkali metal oxide can vary from 4:1 to 2.5:1, with a ratio of roughly 3.2:1 of silicon dioxide to alkali metal oxide being generally preferred. However, alkali metal

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silicate glasses prepared by other routes are equally useful in practicing the present invention and the ratio of SiO_2 to alkali metal salt may be changed to produce silicate compositions with varying properties.

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Preferred embodiments of this invention include preparations of silicate compositions from sodium, lithium, or potassium silicate with the use of sodium silicate being most preferred due to its low cost and availability. Silicate compositions from lithium are preferred to decrease solubility with respect to water.

10

For the present invention preferred embodiments encompass alkali silicates that contain from about 40% to about 80% water by weight. Alkali silicates that comprise from about 50% to about 70% water by weight are even more preferred and the most preferred alkali silicate that comprise from about 55% to about 65% water by weight with 59% being optimal.

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The silicate solution refers to an aqueous solution of alkali silicate. When the silicate solution contains urea, this solution may be prepared by adding a small amount of a very concentrated aqueous solution of urea to an alkali silicate solution. For example, a solution could be prepared which is 0.5% of a 50:50 solution of urea and water and 99.5% of an alkali silicate solution. In certain applications, urea serves to improve the hardness and solidification characteristics. In other applications urea does not appear to play an important role. Urea contents up to about 50% have been tried, however, at higher concentrations the urea causes a breakdown in the alkali silicates. For most aspects of the present invention it will be preferred to use urea concentrations of less than about 1% by weight, with less than about 0.25% by weight of urea being more preferred and typically it would be preferred to not go below a

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urea content of 0.1%. However, for applications desiring to produce a semipermanent product, e.g., for application to the ground to produce a semipermanent cap of the soil, higher concentrations will be preferred as this higher
5 urea content increases the degradability of the silicate compositions.

Almost any type of acid appears to work, including Lewis acids, organic acids and inorganic acids. As used
10 herein the term "aluminum-containing Lewis acid" refers to a Lewis acid that contains aluminum. A Lewis acid is a substance that interacts strongly with an electron pair to form a bond, often referred to as an electron pair acceptor. Aluminum-containing Lewis acids when added to
15 the silicate solution will cause the formation of a gel, as the aluminum atom can interact with lone pairs of the negatively charged silicate oxygen atoms and can be easily incorporated into polymeric silicate structures. However, it would be comprehended by one of skill in the
20 art in light of the present disclosure to vary the Lewis acid to other aluminum-containing species not listed as well as to other Lewis bases containing aluminum such as aluminum oxide and aluminum hydroxide.

25 The aluminum compositions generally include an appropriate solvent, such as water, a polar organic solvent or a combination of these, depending on the characteristics of solidification desired, i.e. strength, solubility, density. Representative classes of polar
30 organic solvents include alcohols, ethers, glycol ethers, ethoxides and ketones. Representative examples of suitable alcohols include tert-butyl alcohol, glycerin, and isopropanol. A representative example of a suitable ketone is methyl ethyl ketone. The preferred solvent for
35 most applications is an alcohol or a mixture of alcohol and water with the preferred ratio of the silicate solution to isopropanol being from about 4 to 1 to about

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9 to 1. The use of alcohol produces silicate compositions that are less expensive, or hard, and cure easily.

5 A preferred embodiment of the present invention is the preparation of silicate compositions utilizing the aluminum-containing Lewis acids aluminum sulfate, aluminum chloride, aluminum nitrate, aluminum fluoride, or aluminum bromide, with aluminum sulfate being the most
10 preferred. However, it would be comprehended by one of skill in the art in light of the present disclosure to vary the Lewis acid to other aluminum-containing species not listed as well as to other Lewis bases containing aluminum such as aluminum oxide and aluminum hydroxide.

15 A key factor in the production of the silicate composition is the very small amount of aluminum compound employed. The inventor has found that the concentration of the aluminum-containing Lewis acid has a profound
20 impact on the cohesiveness of the silicate composition. For instance, at higher aluminum concentrations the silicate composition will not be a cohesive gel but instead will fracture into small pellets that will decompose into a powder with further processing or
25 curing. Although not wishing to be bound by any theories, the aluminum can be viewed as providing a nucleation site for the silicate crystals. Therefore, too many of these sites would lead to a rapid polymerization of the silicates and metasilicates to
30 an amorphous glass that would have to be calcined to produce a vitrified material.

A preferred embodiment of the present invention is the preparation of a silicate composition containing less
35 than about 5% by weight of aluminum. A more preferred silicate composition comprises less than about 3% by weight of aluminum. An even more preferred silicate

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composition contains less than about 1% by weight of aluminum. A more preferred embodiment of the present invention constitutes from about 0.001% to about 1% by weight of aluminum in the silicate composition. The most
5 preferred silicate composition contains about 0.03% by weight of aluminum. These compositions are calculated based on the percent of aluminum.

A preferred embodiment of the present invention is a
10 method of preparing a silicate composition and further dewatering that composition. A more preferred embodiment is the method of preparing a dewatered silicate composition by mechanically dewatering that composition.

15 In this aspect of the invention the term "dewatering" refers to the process of reducing the moisture content of the silicate composition. This process can be accomplished thermally or mechanically or by subjecting the sample to reduced pressures or by a
20 combination of these as well as by other processes that would be known by one of skill in the art. Generally it is preferred to do this dewatering at ambient temperatures although this process can occur at from slightly above freezing to about 90 to 100°F. At these
25 higher temperatures the silicate composition becomes almost plastic like and is difficult to process. If the composition is dewatered thermally, it is preferred to accomplish this in a controlled way, such as by heating it only slightly to about 90 or 100°F or by air drying it
30 with a stream of hot, dry air. As used herein the term "mechanical dewatering" refers to the process of reducing the moisture content of a material by physically manipulating said material, for instance with an opposing belt or turn screw dewatering system or a cheese cloth
35 press or by wringing it.

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An even more preferred embodiment is to mechanically dewater the silicate composition at from about 65°F to about 75°F.

5 In other embodiments, silicate compositions can be prepared containing a variety of materials which impart special properties to the silicate compositions formed. Organic materials can be plastic resins, such as
10 polyesters, nylon, polyethylene and polypropylene; simple organics, such as benzene and gasoline; and cellulose and its derivatives. The addition of polyester is particularly preferred for certain applications. For
15 example, if the silicate composition is going to be used for the preparation of a foam, the addition of polyester increases the resiliency and strength of the foam.

 Inorganic compounds include metallic oxides, such as iron oxide, bismuth trioxide; metals, such as aluminum, copper, boron, iron, lead, heavy metals; and inorganic
20 salts, such as copper sulfate, sodium sulfates and bisulfates.

 Another aspect of this invention improves water resistance. Addition of a metal oxide in combination
25 with a polar organic solvent during preparation of the final composition reduces the solubility of the resultant material with respect to water, a common environmental component responsible for natural erosion. The addition of the metal oxide in combination with the polar organic
30 solvent serves to facillitate production of homogenous, uniform compositions, as opposed to granular compositions lacking uniformity of composition. The metal oxide is primarily present to exchange its metal ion (e.g., calcium or magnesium) for a sodium, potassium or lithium
35 ion to produce a less soluble metal silicate. Generally, the metal oxide is added in an amount up to about 15% based on the total weight of the starting materials,

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including water and polar organic solvent. The polar organic solvent is believed to prevent formation of metal oxide-alkali silicate interaction prior to complete mixing. Methods for mixing the starting materials are well known and may be found in commonly available chemical engineering references such as Perry's Chemical Engineers Handbook, 6th ed., McGraw Hill 1984, New York, New York. The polar organic solvent, which is at least partially miscible in water, is important in introducing the metal oxide, or the acid, prior to mixing or combining with the silicate solution.

A more preferred embodiment is the method of making a silicate composition wherein the material added to the urea/silicate solution as a radiation blocker. As used herein the term "radiation blocker" refers to a chemical compound that is capable of absorbing, or shielding against, α , β , γ , or X-rays. Such compounds include bismuth oxide and lead oxide.

20

Preferred embodiments also include the various silicate compositions of matter with and without the presence of organic and inorganic additives.

Another aspect of the present disclosure is a method of vitrifying a waste material by heating a silicate composition until it becomes sufficiently molten to be flowable, mixing the molten composition and the waste material, and cooling the mixture to vitrify the waste material.

30

As used herein the term "waste" or "waste material" refers to any material of which it is desired to encapsulate for the purposes of storage, handling or transportation. These waste materials may contain radioactive, toxic or flammable materials; organic or inorganic compounds; solids, such as soils, sludges,

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particulate matter, and metals; liquids, such as clear effluents like water, or gases, such as hydrogen. These examples should not be construed as providing limitation as the silicate compositions described have not rejected
5 any waste materials that have been tried.

In the present invention the terms "glassify" and "glassification" refer to the forming of a water resistant waste containing solid. This is accomplished
10 by encapsulating it in a silicate composition with appropriate additives as described above. It is generally preferred to not have in excess of 30% loading of waste materials into the glassified product. It is also preferred to allow this process to occur to from
15 about several days to about 12 months. This process is referred to as a cold process to distinguish it from processes that require heating of the waste containing silica material either thermally or by microwave radiation generally to at least several hundred degrees
20 Fahrenheit.

Although the encapsulation of the waste can occur at ambient temperatures, it is necessary to form an intimate mixture, or homogeneous blend, of the waste and the
25 silicate composition to ensure homogeneity in the glassified product. As the silicate composition will appear stiff at room temperature, it is necessary that the silicate composition be sufficiently molten to be flowable. This usually requires the temperature of the
30 silicate composition to be from about 50 to about 150°F depending on the specific characteristics of the silicate composition.

A preferred embodiment of this aspect of the
35 invention is the vitrification of radioactive waste materials. An even more preferred embodiment is the vitrification of radioactive waste materials employing

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silicate compositions containing radiation blockers. Although the silicate composition is itself a radiation blocker, it would be advantageous to enhance this quality in the glassified waste product to further enhance the safety of handling, transporting, and storing these wastes.

The present invention also provides a continuous flow process using microwave radiation and no hazardous or volatile chemicals for making a foam-like material that can be composited with numerous organic and inorganic materials to create a wide variety of materials of differing characteristics. This foam is envisioned to be useful in the construction of materials for use as building products, thermal and acoustic barrier materials, radioactive or electromagnetic shielding materials, and electronic components; in the production of controlled and uncontrolled energy; and in refrigeration.

20

An embodiment of the present invention is a method of making a silicate foam composition. This method comprises preparing from a silicate composition that has been dewatered, preferably to contain from about 20% to about 30% moisture, and subjecting this material to microwave radiation. The material will be cured by allowing it to cool to ambient temperatures to form the foam.

In the present invention the term "silicate foam" or "foam" refers to materials that have been prepared in accordance with the above mentioned procedure. "Composites" of the foam are prepared by mixing the additives with a silicate solution and then radiating with microwave radiation the silicate compositions containing organic and inorganic materials.

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Another embodiment of the present invention is preparing a granular material by fracturing the silicate composition under a flow of dry air. The foams are prepared under a flow of dry air to facilitate the formation of free flowing granules. This air may also be any inert gas, however, air is preferred because it is economical, nonflammable, and nontoxic. The air may be any temperature but temperatures from about 120 to about 200°F are preferred.

10

The present invention also encompasses the foam and its composites that are produced in accordance with the above mentioned method.

15

Other distinctions from prior methods to produce foam include composition parameters, curing and treatment conditions necessary to produce desired qualities in the finished product. It has been discovered by the present inventors that additions of materials such as metal oxides which seem to interfere with the plasticity of the sol gel which is to be foamed have a pronounced effect on foam suitability include any materials that inhibit the plasticity of the sol gel material to be foamed. Also, solvents or water which remain in the sol gel material prior to application of heat play an important role in the amount of expansion that can be expected during the foaming process. Steps that are taken to dewater the starting material or cure the sol gel prior to foaming need to be controlled carefully to insure homogenous results between foam productions.

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Microwave radiation plays an important role in foam making because this type of radiation are distributed more equally throughout the sol gel starting material than conventional heat sources. If conventional heat sources are employed, steps are needed to insure uniformity in applying the heat throughout the sol gel

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starting materials to insure that uneven expansion does not occur as the foaming process tends to be irreversible.

5 The present invention also provides a method for solidifying aqueous solutions into a cohesive water resistant calcium silicate matrix within minutes. This method utilizes a two component chemical system designed to quick-set water based materials, such as radioactive
10 waters and hazardous aqueous chemicals, into a stable solid without a drastic increase in volume. This process will result in substantial increases in public safety and decreases in cost in the transportation and storage of contaminated liquid wastes, particularly radioactive
15 effluents. Current technology relies on cementaceous materials and processes that often encapsulate water with large volume and weight increases. Depending on the desired strength of the end product, as little as 15% by volume of this product can be used to instantly solidify
20 aqueous solutions into a stable solid form.

 Another aspect of the present invention is a method for solidifying an aqueous solution by adding the calcium silicate or Portland cement #2 to the aqueous solution
25 and subsequently adding to this solution, which is preferably 10 to 15% by volume of calcium silicate or Portland cement #2, a solution of sodium silicate and urea, in an amount to effect a 3 to 5% increase in volume being preferred, to form a solid. The calcium silicate
30 or Portland cement #2 will generally not be totally dissolved in the aqueous solution but will instead form a finely dispersed powder with agitation. In order to get homogeneous solids it is important to agitate the dispersion during this process, by stirring for instance,
35 to keep the calcium silicate or Portland cement #2 from settling and the dispersion from forming a liquid layer on top of the solid. Normally, the solidification

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process is immediately apparent upon addition of the urea/silicate solution, and within one hour the material will be set. At this time it is necessary to store the product in a sealed container until it is fully cured or
5 it will disintegrate into dust.

The "aqueous solution" may contain waste materials, including sludges, particulate matter, and sodium compounds. The present method will be particularly
10 useful in the solidification of tritiated water that is produced during the cooling of spent reactor core rods from civilian reactors.

Another embodiment of this invention is the method
15 of solidifying an aqueous solution and then heating the resultant solid to ceramic temperatures. As used herein the term "ceramic temperatures" refers to temperatures high enough to produce ceramic materials, approximately 1600-1800°F. This aspect would be preferred in instances
20 where one was vitrifying high-level radioactive clear effluents. These effluents could first be solidified and then allowed to disintegrate. It would then be advantageous to either heat it to ceramic temperatures to effect a "hot" vitrification or to encapsulate the powder
25 into the silicate composition via a "cold" process.

In another aspect, the present invention contemplates a kit for the solidification of aqueous wastes. Said kit can contain a calcium silicate or
30 Portland cement #2 and a separately packaged aqueous solution of sodium silicate and urea. The kits of the present invention will typically include a means of containing the calcium silicate and aqueous urea/sodium silicate solution in close confinement for commercial
35 sale. Such containers may include injection or blow-molded plastic containers into which the two compositions are retained.

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One skilled in the art would recognize in light of the present disclosure that although the specified materials and conditions are important in practicing the invention, unspecified materials and conditions are not
5 excluded as long as they do not prevent the benefits of the invention from being realized.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 The present invention encompasses a process designed to eliminate the need for heat and energy input in the encapsulation of water and particles by the process of chemical crystallization and solidification. A principal use for this process is in the encapsulation of hazardous
15 contaminated waters, particularly radioactive waters. This process allows for the solidification of radioactive materials, including waters, sludges, contaminated soils, and even gases, at room temperatures either in place or through an industrial processing technique.

20

This process for vitrifying wastes at ambient temperatures involves encapsulating a waste material into a silicate composition and allowing this mixture to cure into a water resistant solid. The silicate composition
25 is prepared by reacting an aqueous alkali silicate solution with an aluminum-containing Lewis acid. The preferred alkali silicate is sodium, however, one skilled in the art would recognize that other alkali silicates may be useful depending on the properties desired in the
30 final glass and the waste to be encapsulated.

The sodium silicate glass and aqueous solution can be prepared according to procedures well known in the art with the preferred sodium silicate corresponding to grade
35 41 commercial sodium silicate. This preparation involves the formation of a melt of silicon dioxide and soda ash which is subsequently cooled and the dissolution of this

- 22 -

glass into water to form an aqueous sodium silicate. The aqueous sodium silicate can contain between 40 and 80% water although 59% is preferred. A urea/silicate solution, Solution A, is formed by mixing 99.5% of the aqueous sodium silicate and 0.5% of a 50:50 solution of urea:water.

After the sodium silicate glass dissolves into a viscous aqueous liquid, the chemical fusion mixing stage begins. At this point the acid is added. The acid can be a wide variety of acids including both organic and inorganic acids, including Lewis acids. An aluminum-containing Lewis acid can be such compounds as aluminum sulfate, aluminum chloride, aluminum fluoride, aluminum nitrate, or aluminum bromide, aluminum sulfate being the most preferred. However, it would be understood by one of skill in the art in light of the present disclosure to vary the Lewis acid to other aluminum-containing species not listed as well as to other Lewis bases containing aluminum such as aluminum oxide and aluminum hydroxide. The acid is generally either diluted with or dissolved in an appropriate solvent, such as water, a polar organic solvent such as a ketone, an ether, a glycol ether, an ethoxide, an alcohol, or a combination of these, and the like, depending on the characteristics of crystallization desired, i.e. strength, solubility, density. A representative example of a suitable ketone is methyl ethyl ketone. Representative examples of suitable alcohols include isopropanol, glycerin and tert-butyl alcohol. The preferred solvent for most applications is a mixture of an alcohol and water.

Once the chemicals are injected and thoroughly mixed within the chemical fusion mixing station, a gelling process will occur either instantaneously or over a period of time, i.e. hours or days. The preferred reaction time depends on the precise silicate composition

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and its anticipated use. It is necessary to avoid temperatures near freezing or approaching boiling with the preferred reaction temperature being about 25°C. The preferred percentage of aluminum species to liquid glass solution is less than 0.5% by weight.

A key factor in the production of this silicate composition is the very small amount of aluminum sulfate employed. The previous references teach to the use of much higher aluminum concentrations. For example, Pope et al. in U.S. Patent 4,376,070 teaches the use of up to 30% of aluminum compounds and that the higher silica and alumina glasses should be more resistant to fracturing. Surprisingly, the inventor has found that if higher than 5% concentrations of aluminum sulfate are used, the final product will not be a cohesive silicate composition but instead will fracture into small pellets that will decompose into a powder with further processing or curing. This is supported by Brownell et al. who teach the use of relatively high aluminum concentrations in the encapsulation of cesium, 25% molar ratio to silicon and cesium; they report that their final product was a solid with a very fine crystal size.

Although not wishing to be bound by any theories, it is believed that the higher concentrations of aluminum sulfate cause a rapid polymerization of the silicates and metallosilicates to an amorphous glass that must be further calcined to produce a glassified material. However, the present invention provides a more delicate way to initiate solidification and crystallization than in the known methods by adding much lower amounts of the aluminum-containing Lewis acid. Therefore, although relatively longer cure times are required, heating, or calcination, is not a requisite for forming a glassified product.

- 24 -

After roughly 90% by volume of the reaction mixture is contained in the rubbery silicate composition, this mass can be subjected to a "dewatering" step with a "mechanical dewatering" being preferred. This can be accomplished by procedures that are well known in the art, such as an opposing belt or turn screw dewatering system or a cheese cloth press. The percentage of water entrained within the silicate composition will vary from about 15 to about 35%. Practical concentrations for most industrial uses will range from 20-30% with the most preferred being 25% encapsulated water in the finished solid. Moisture content can be estimated by comparing the viscosity of the silicate composition to standard viscosity curves. Additionally, if a sample is dehydrated below the desired level, it is possible to rehydrate the silicate composition by exposure to water. Such rehydration preferably occurring within 24 hours.

The silicate composition is now ready to be used in the encapsulation of waste materials. This process involves the formation of an intimate mixture of a sufficiently molten silicate composition with the desired waste material. This silicate can encapsulate solids, liquids, and gases both organic and inorganic. It is surprisingly able to accommodate high concentrations of sodium, corrosives, and weak acids. After a suitable "curing", the finished product will be a water and waste encapsulated silicate crystal matrix that will be stable and water resistant for the proper transport and disposal of contaminated waste.

Although the silicate composition is an effective radiation blocker, other blockers, such as bismuth oxide and lead oxide, can also be incorporated into the silicate for the vitrification of radioactive wastes. The silicate composition can also be used for various other applications, such as dust control by spray

- 25 -

application of the molten silicate to the soil, vitrification of contaminated soils into a non-leaching solid state by injection into the ground, the building of underground barriers to prevent migrations of contaminated waters, the strengthening of underground storage facilities, the building of materials that require a "cold pour" application, and the like.

The silicate composition can also be used in the production of foams. In this embodiment, the present invention also encompasses a continuous flow process with no hazardous or volatile chemicals for making a material that can be composited with numerous organic and inorganic materials to create a wide variety of materials of differing characteristics. This foam is envisioned in the construction of materials for such uses as building products, thermal and acoustic barrier materials, radioactive or electromagnetic shielding materials, and electronic components; and in radio transmissions, controlled and uncontrolled energy production and refrigeration.

The foam is manufactured by rapidly and mechanically fracturing the silicate composition while it is still rubbery, with a moisture content of from 15 to 35% with the preferred moisture content being 25-26%, into a free flowing granular material. Another method is to granularize the silicate composition under a flow of dry, preferably hot 120 to 200°F, air. The granular material is then subjected to microwave radiation for several minutes until all the moisture is driven off as evidenced by the ceasing of the expansion of the material. The foam can also be partially dehydrated by microwave radiation and molded prior to the total dehydration or hardening. The foam is then allowed to cool.

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The preferred granular size is having a diameter less than one millimeter. Larger granules may not experience a homogeneous expansion when subjected to microwave radiation and is therefore not desired. It is possible to subject the granules to microwave radiation while they are in a mold, if a specific shape is required, or while run through two opposing rolls of foil to produce a sheet.

10 The silicate foam is composed of cavities, caused by the rapid expansion and evaporation of the water and/or solvent molecules by the microwave radiation.

15 The present invention also encompasses the composites of this foam. These composites are produced by adding the desired composite material to the urea/silicate solution, solution A, prior to the chemical fusion mixing stage. Dramatic and surprising changes in properties are often observed with the incorporation of only a few percent by volume of the material to be composited to solution A, however, it is possible to add up to 50% of composite into solution A.

25 The present invention also discloses a method for solidifying an aqueous solution. This method utilizes a two component chemical system designed to quick-set water based materials, such as radioactive waters and hazardous aqueous chemicals into a solid without a drastic increase in volume. This process will result in substantial increases in public safety and decreases in cost in the transportation of wastes as a solid rather than a liquid. It is envisioned that this product will be particularly useful in the solidification of tritiated water that is produced during the cooling of spent reactor core rods from civilian reactors. Current technology relies on cementaceous materials and processes that often encapsulate water with large volume and weight increases.

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By contrast, depending on the desired strength of the end product, as little as 15% by volume of this product can be used to instantly solidify into a stable solid form. This compares very favorably to ordinary cementaceous processes which require an increase in volume of 1000% to 2000% in the solidification of aqueous wastes. It can also be used to solidify sludges and particulate matter and can surprisingly accommodate wastes with exceedingly high sodium concentrations, up to 50% sodium compounds and very alkaline solutions.

The first component is solution A and the second component a calcium silicate powder or Portland cement #2. The solidification process involves addition of the powder, 10 to 12% volume increase on addition is preferred, to the aqueous waste and stirring the mixture until the solid is finely dispersed. Solution A is then added with stirring to give up to a 10% increase in volume with a 3 to 5% increase being preferred. A solidification process is immediately apparent and within one hour the material has set. At this time it is necessary to store the product in a sealed container or it will disintegrate into dust.

The use of powders with higher percentages of calcium carbonate tends to produce vitrified products with very low compression strengths while those with lower concentrations of calcium carbonate require large increases in volume to obtain a solid. Generally the silica and iron oxide act as hardeners to increase the compression strength of the vitrified products.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although any methods and materials similar or equivalent to those described

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herein can be used in the practice or testing of the present invention, the preferred methods and materials are now described. Unless mentioned otherwise, the techniques employed herein are standard methodologies well known to one of ordinary skill in the art.

EXAMPLE 1: Materials and Methods

All solvents and reagents were of reagent grade quality, available commercially, and were used without further purification. All percent compositions were computed by weight unless otherwise specified.

EXAMPLE 2: Preparation of Solution A

Solution A was formed by making a solution of 99.5% sodium silicate (grade 42) and 0.5% of a 50:50 solution of urea:water. Solution A cannot be stored in contact with zinc, copper, brass, or aluminum for any length of time as they will react with the solution over the course of days. The preferred storage material is cold rolled steel or more preferred in polyplastic tanks.

The synthesis of sodium silicate glass is generally known in the art and the parameters of its preparation can be varied in ways that are generally known to one of skill in the art depending on the properties desired in the final product. Although sodium silicate glass was employed in the present invention, it would be understood by one of skill in the art to employ other alkali silicate glasses depending on the desired properties of the final product.

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EXAMPLE 3: Preparation of a Silicate Composition

A slurry was prepared by partially dissolving 0.47 g $\text{Al}_2(\text{SO}_4)_3$ in 0.5 g of water. This solution was diluted with 5 g of isopropyl alcohol and 5 g of water, "solution B". Solution B was then added with constant stirring to 90.68 g solution A. A cohesive gel began forming immediately. After several minutes roughly 90% by volume of the mixture was contained in a rubbery cohesive mass. This mass was then mechanically dewatered to a moisture content of roughly 30%.

A solution was prepared by partially dissolving 10 g of $\text{Al}_2(\text{SO}_4)_3$ in 15 g of water. This mixture was then added with stirring to 100 ml of Solution A. Instead of a cohesive gel, small granular pellets were formed. These pellets dried to a fine powder within a few days. This observation explains the failure of the known methods to obtain a glass at low temperatures that is useful for the encapsulation of waste materials as the excess aluminum sulfate causes fracturing in the formation of the glass to a powder. This is also the case when a silicate composition containing an excess Lewis acid is used for the glassification of wastes.

EXAMPLE 4: Cold Glass Encapsulation of Water and Particles

It is envisioned that the present invention will be useful in the encapsulation of hazardous contaminated waters, particularly radioactive waters, soils, solids, sludges, and even gases at room temperatures. For this application, the silicate composition which appears stiff at room temperature must be heated until it is sufficiently molten to be flowable, roughly 40-150°F with 90-100°F being preferred. Once it is a flowable mass it can be injected into a mixer system, such as a ribbon

- 30 -

blender or turn screw mixer, and combined with the waste material, which can be a solid, liquid or gas. The silicate composition is able to accommodate up to 30% loading of waste, organic or inorganic, by volume. This composition has also been used to encapsulate hydrogen gas. Another surprising result was the ability of this composition to incorporate wastes with very high sodium nitrate concentrations (80-90%), similar to wastes generated at the Hanford Nuclear Reservation site, with extremely high loadings of up to 30%, as well as acids and corrosives, such as hydrochloric, nitric, and sulfuric acids. However, for high-level radioactive wastes of cesium, plutonium, and uranium a preferred loading will be 0.5 to 1% by volume.

15

The next step is the "curing" of the glass encapsulated waste into a solid. The solidification process will be apparent immediately after mixing and will continue for several hours. At this point although the glass will be appear to be a solid the actual crystallization process to a solid will take from months to years depending on the waste material encapsulated. For proper "curing" the encapsulated waste should be kept at from 40-120°F with 40-60°F being preferred. The longer the "curing" time at this temperature the more stable the crystalline matrix will be. Generally the curing process takes from 3 to 6 months with an initial cooling to 40-60°F for several days and then storage below 70°F for the remainder of the curing process being preferred. Additives may be employed to accelerate the curing process.

25
30

EXAMPLE 5: Preparation a Silicate Foam and Its Composites

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The foam of the present invention is a silica based crystalline material with extraordinary properties, such

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as low density, low thermal conductivity, inflammability, radiation and cosmic ray shielding ability, and environmental degradability and compatibility. The inflammability and low thermal conductivity of this foam were demonstrated by heating a piece of the foam with a propane flame for 5 minutes. The surface temperature of the foam immediately after removing the flame was only raised by a few degrees. No burning or apparent decomposition were observed.

10

Additionally, the foam's ability to form composites with a wide variety of organic and inorganic composites enhances its versatility in forming materials with a broad range of properties and characteristics. This versatility will allow this foam and its composites to be used in the construction of materials such as for use as building products, thermal and acoustic barrier materials, radioactive or electromagnetic shielding materials, electronic component, controlled and uncontrolled energy production and refrigeration and the like.

20

Preparation of a Silicate Foam

25

A freshly prepared piece of the silicate composition, 1" x 2" x 0.5", was fractured into small pieces, all but a few had a radius less than 1mm, and dried under a stream of hot air. The pieces were then immediately subjected to microwave radiation until the material ceased expanding in size to produce a light-weight solid, the silicate foam. The hardened foam had a number of holes and defects caused by the nonuniform expansion of the water in the larger granules.

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TABLE I. PROPERTIES OF THE SILICATE FOAM AND REPRESENTATIVE COMPOSITES

Composite	Properties
None	Low density, low thermal conductivity, total inflammability, radiation and cosmic ray shielding ability, and environmental degradability and compatibility.
5 Citric acid:sodium bisulfate 1:1	Increased hardness, resistant to solubility in water, light weight, adjustable compression strength (eg. 0.8% composite - compression strength of 10 psi, 2.7% - compression strength >100 psi).
BiO ₃	Enhanced radiation blocker.
10 Polyester 0.5%	Dramatic increase in resiliency, capable of holding commercial fasteners such as nails and screws.

Preparation of Composites

15 To form composites with this foam the desired composite was added to the mixture of solution A and the aluminum sulfate containing solution. Materials known to form composites with this silicate foam include plastic resins, such as polyesters, nylon, polyethylene and

20 polypropylene; simple organics, such as benzene and gasoline; cellulose and its derivatives; and inorganics - metallic oxides, such as iron oxide, bismuth trioxide; metals, i.e. aluminum, copper, boron, iron, lead, heavy metals; and inorganic salts, such as copper sulfate,

25 sodium sulfates and bisulfates. Some representative foams and their properties are listed in Table I. By way of illustration, the properties of the polyester composite were very surprising in that as little as 0.5% of

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polyester imparted increased resiliency and strength and the ability to use fasteners such as nails and screws.

5 **EXAMPLE 6: Calcium Silicates for the Solidification of Aqueous Solutions**

10 The present invention encompasses a two component system designed to quick-set water based materials, such as radioactive waters and hazardous aqueous chemicals into a stable solid. Depending on the desired strength of the end product, aqueous solutions can be instantly solidified into a stable solid form accompanied with as little as a 15% increase in volume.

15 Experiment

To 100 ml water enough calcium silicate powder was added to effect a 10% increase in volume. The resultant slurry was vigorously stirred until the powder was finely dispersed. 10 ml of solution A was added while stirring continued. The solution instantly thickened and was completely hardened in minutes. The total increase in volume was approximately 20%.

25 A particularly useful embodiment of the present invention employs the use of metal oxides and a Lewis acid in a polar solvent as one component in a two part mixture and an alkali silicate as the other component. The following examples 7-12 take advantage of a polar solvent that prevent immediate reaction between the constituents of the mixture prior to obtaining a homogenous mixture. Throughout the examples, several desirable qualities were observed and were found to be helpful in determining the usefulness and applicability of differing polar organic solvents. The higher molecular weight alcohols (e.g. glycerin) reacted less vigorously with the alkali silicates to form gels while the lower molecular weight alcohols (e.g., isopropanol)

- 34 -

caused faster reactions between the metal oxides and the alkali silicates as well as shorter gellation times. This result showed that heavier alcohols tended to be better for prevention of premature reactions while the lighter alcohols could be employed to hasten the reactions. Steric effects were also noted. The more sterically hindered compounds seemed to react more like the heavier compounds without significant additional weight (e.g. t-butyl alcohol vs. isopropanol). Also, it was noted that more soluble metal oxides were faster reacting than less soluble ones (e.g., CaO vs. MgO) and with increased amounts of metal oxides, the production of foams was inhibited.

15 **EXAMPLE 7**

10 g of powdered CaO and 20 g of 325 mesh low reactive MgO are mixed together with 5 g of powdered $\text{AlSO}_4 \times \text{H}_2\text{O}$ (commercial grade). This dry material is then added to 40 ml of glycerin and stirred thoroughly. This slurry is then added to 60 ml of sodium silicate (grade 41). The mixture is quickly and thoroughly mixed. After about 2-3 minutes, it begins to harden and results in a fairly hard solid within about 10 minutes. After curing for two to three weeks at room temperature the material was cut with a saw and one quarter part was tested for solubility in water. The pat that was tested weighed 53.35 g prior to treatment and 34.25 g after treatment losing about 36% of its initial weight without suffering any appreciable loss in volume or change in form or shape.

The solubility test consisted of boiling the piece in water which was constantly replaced using a 1 l beaker and sufficient water to keep the material covered for 72 hours. Periodically, once to two times a day the water was completely replaced to avoid any possibility of

- 35 -

salting out the water which could prevent further dissolution. After boiling, the test piece was retrieved, and the piece was dried in an oven at 170°-200°F for 24 hours and then weighed.

.5

Analysis of the material showed that most of the weight loss, if not all, was from glycerin and water that had not previously evaporated during curing time (e.g., water and glycerin content by% wt were initially 66% of total weight).

10

EXAMPLE 8

A polar solvent, a metal oxide and an alkali silicate were combined to produce a solid material using procedures described in example 7. The polar solvent was t-butyl alcohol (40 mL), the metal oxide was MgO (10 g), and 90 ml of sodium silicate (grade 42) was used. The resulting solid was boiled in water and found to be resistant to dissolution in water. The presence of the Lewis acid as opposed to a Lewis base, which is also a metal oxide, was examined in this example. It was found that for curing and solidification purposes the metal oxide could be used to replace the Lewis acid with favorable results.

25

EXAMPLE 9

The procedure of Example 7 was repeated using 40 ml of glycerine solvent, 25 g of MgO, 10 g of $\text{AlSO}_4 \times \text{H}_2\text{O}$ and 90 ml of sodium silicate (42). The resulting solid was tested in boiling water and found to be resistant to dissolution in water.

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EXAMPLE 10

The procedure of Example 7 was repeated using 40 ml of glycerin solvent, 10 g of CaO, 25 g of MgO, 10 g of
5 $\text{AlSO}_4 \times \text{H}_2\text{O}$ and 90 ml of sodium silicate (42). During the 10 minute hardening phase the material was split in two parts and 40 ml t-butyl alcohol was added which significantly increased the rate of hardening. The resultant material lost all characteristics of
10 plasticity.

EXAMPLE 11

The procedure of Example 7 was repeated using 40 ml
15 of glycerin solvent, 10 g of MgO, 25 g of $\text{AlSO}_4 \times \text{H}_2\text{O}$, and 90 ml of sodium silicate (42). Again, the sample was split during the 10 minute hardening phase and half was added to 40 ml of t-butyl alcohol. This material became very crystalline and crumbly and did not make a good
20 solid for purposes of encapsulation. Here, it is seen that there is a practical upper bound for the amount of a Lewis acid. This upper bound is around 15% AlSO_4 on an anhydrous basis, this percentage based on the total weight of the starting reactants including water and polar
25 organic solvent. Amounts much exceeding 5% quickly lose their cohesive properties.

EXAMPLE 12

30 The procedure of Example 7 was repeated using 60 ml of glycerin, 40 ml of t-butyl alcohol, and 10 g of CaO. This solution (partially a slurry) was made first by combining the above materials and then further adding 15 g CaO. From the resultant solution 30 ml was taken and
35 added to 90 ml of sodium silicate (42). This resultant material hardened into a white mass which was allowed to cure for several months before it became very water

- 37 -

resistant and hard. During the curing time the material was still fairly soft to touch.

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It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications in light thereof will be

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suggested to persons skilled in the art and are to be included within the spirit and purview of this application and scope of the appended claims.

- 40 -

CLAIMS:

1. A method of preparing a silicate composition,
comprising the steps of:

5

(a) preparing an aqueous silicate solution
comprising an alkali silicate and, optionally,
urea;

10

(b) adding to the aqueous silicate solution a
mixture comprising an acid and a polar organic
solvent to form an admixture; and

15

(c) mixing the admixture to form the silicate
composition.

20

2. The method of claim 1, wherein the polar organic
solvent is an alcohol or a ketone.

3. The method of claim 2, wherein the ratio of silicate
solution to the polar organic solvent by volume is from
about 4 to 1 to about 9 to 1.

25

4. The method of claim 1, further comprising dewatering
the silicate composition.

30

5. The method of claim 1, wherein the alkali silicate
is sodium, lithium, or potassium silicate.

35

6. The method of claim 5, wherein the alkali silicate
composition is sodium silicate.

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7. The method of claim 1, wherein the alkali silicate comprises from about 40% to about 80% water by weight.

5 8. The method of claim 7, wherein the alkali silicate comprises from about 50% to about 70% water by weight.

10 9. The method of claim 8, wherein the alkali silicate comprises from about 55% to about 65% water by weight.

15 10. The method of claim 1, wherein the silicate solution contains urea in an amount less than about 50% by weight.

11. The method of claim 10, wherein the silicate solution comprises less than about 2% by weight of urea.

20 12. The method of claim 11, wherein the silicate solution comprises from about 0.1 to about 1% by weight of urea.

25 13. The method of claim 12, wherein the silicate solution comprises 0% by weight of urea.

30 14. The method of claim 1, wherein the acid is aluminum sulfate, aluminum chloride, aluminum fluoride, aluminum nitrate, or aluminum bromide.

35 15. The method of claim 14, wherein the acid is aluminum sulfate.

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16. The method of claim 1, wherein the silicate composition comprises less than about 5% by weight of aluminum.

5

17. The method of claim 16, wherein the silicate composition comprises less than about 3% by weight of aluminum.

10

18. The method of claim 17, wherein the silicate composition comprises less than about 1% by weight of aluminum.

15

19. The method of claim 18, wherein the silicate composition comprises from about 0.001% to about 1% by weight of aluminum.

20

20. The method of claim 4, wherein the silicate composition is mechanically dewatered.

25

21. The method of claim 20, wherein the silicate composition is mechanically dewatered at from about 25°C.

30

22. The method of claim 1, further comprising adding an inorganic material to the mixture.

35

23. The method of claim 22, wherein the inorganic material is a iron oxide, a metal, or a salt.

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24. The method of claim 4, further comprising adding a radiation blocker to the mixture.

5 25. The method of claim 4, further comprising adding an organic material to the silicate solution.

10 26. The method of claim 25, wherein an organic material is a plastic resin, a simple organic, cellulose, or a derivative of cellulose.

15 27. The method of claim 26, wherein the plastic resin is polyester.

20 28. The method of claim 1, where the mixture further comprises a metal oxide.

25 29. The method of claim 1, wherein the mixture further comprises calcium oxide, magnesium oxide or a mixture thereof.

30 30. A composition of matter produced in accordance with the method of claims 1, 2, 4-6, 14, 15 and 22-29.

31. A method of vitrifying a waste material comprising the steps of:

35 (a) heating a silicate composition made in accordance with claim 4 until it becomes sufficiently molten to be flowable;

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(b) mixing the molten composition with the waste material; and

5 (c) cooling the mixture to vitrify the waste material.

32. The method of claim 31, wherein the mixture comprises up to 30% by weight of waste material.
10

33. The method of claim 31, wherein the mixture is cured for from about one day to about 12 months.
15

34. The method of claim 31, wherein the waste material contains radioactive materials.

20 35. The method of claim 34, wherein the silicate composition contains a radiation blocker.

36. The method of claim 1, further comprising layering
25 the silicate composition on the ground.

37. A method of making a silicate foam composition, comprising the steps of:
30

(a) preparing a silicate composition in accordance with claim 4 or claims 22-29; and

35 (b) subjecting the silicate composition to microwave radiation to form the silicate foam composition.

- 45 -

38. The method of claim 37, wherein the silicate composition is fractured under a flow of dry air prior to subjecting the silicate composition to microwave radiation.

5

39. A composition of matter produced in accordance with the method of claim 37.

10

40. A method of preparing a calcium silicate composition comprising the steps of:

15

(a) forming a mixture which comprises from about 80 to about 99% Portland cement #2, less than about 0.5% aluminum sulfate, and less than about 20% iron oxide;

20

(b) adding the mixture to water to form a slurry having a volume which is about 3 to about 5% greater than a starting volume of the water; and

25

(c) adding an aqueous alkali silicate solution containing urea to the slurry, the aqueous alkali silicate solution added in an amount sufficient to increase the volume of the slurry about 5 to about 15%, to solidify the slurry to form the calcium silicate composition.

30

41. The method of claim 40, wherein the mixture comprises from about 75% to about 95% Portland cement #2, and from about 5% to about 15% iron oxide.

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42. A composition of matter produced in accordance with the method of claim 40 or 41.

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(54) Title: COLD PROCESSES FOR PREPARING GLASS THROUGH THE USE OF A CRYSTALLINE SILICATE MATRIX			
(57) Abstract <p>The present invention discloses a process for solid waste encapsulation in forms suitable for long term storage and transportation as well as a process for handling inadvertent toxic or radioactive releases and accidents. The glassification of toxic and radioactive wastes in a stable, water resistant solid by a process that does not require subjecting the waste to harsh conditions of elevated pressures and temperatures or a drastic increase in either volume or weight is described. Novel materials based on this silicate composition are also disclosed.</p>			

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INTERNATIONAL SEARCH REPORT

Inter national Application No

PCT/US 95/08716

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G21F9/16 G21F9/34 G21F9/30 C01B33/16 C04B28/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G21F C01B C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	FR,A,2 527 376 (KERNFORSCHUNGSZENTRUM KARLSRUHE) 25 November 1983 see claims 1,2 see page 3, line 1 - line 31 ---	1-39
Y	DATABASE WPI Week 8836 Derwent Publications Ltd., London, GB; AN 88-254921 & JP,A,63 187 196 (TOSHIBA KK) , 2 August 1988 see abstract --- -/--	1-39

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Date of the actual completion of the international search

22 December 1995

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International Application No

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